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THEORY OF SUPERIONIC CONDUCTORS

Indiana University Foundation

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Theoretical physics research is reported on several aspects of superionic conductors. Theories of ionic conductivity are developed to explain experiments. The role of ion-phonon interaction is explored by the solution of several mathematical models of ion and electron conduction in many-particle systems. →

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A. Summary of Research Effort

Our primary research objective is to understand why some solids have a very high conductivity of ions. Several hundred such materials have been identified. Some have usefulness in chemical devices such as batteries. We do theoretical physics research into the mechanisms of ion motion in solids, in an effort to identify why some solids conduct ions well, while others do not. The Grant funds have been used to support several types of theoretical calculations.

1) Ion Transport

Since high ionic conductivity is the feature which makes these solids have technical applications, it is important to understand the physical mechanisms which limit the motion of ions. The traditional viewpoint is the ion motion is limited by static potential barriers, which the ion can hop over during a thermal fluctuation. Our research has investigated other mechanisms which appear important in good ion conductors, since they have low static potential barriers. Instead, we have investigated dynamic potential barriers, which arise from the motion of the other ions--through phonons or ion-ion correlations.

a) Thermoelectric Power

The thermoelectric power is the electrical voltage produced in a solid by a temperature gradiant. Our theoretical work showed that a measurement of this quantity in superionic conductors, as a function of temperature, provides great insight into the mechanisms of ion transport.

One of the significant accomplishments of the present Grant was Dr. Girvin's important work on the thermoelectric power of superionic conductors. There are two aspects to this work. The first was his efforts to clarify the sign convention of this quantity. The thermoelectric coefficient S is the

1

ratio between the potential difference $\nabla\phi$ which is developed on a solid by the
application of a temperature gradient ∇T

$$\nabla\phi = S\nabla T$$

It may have either sign, but the experimentalists usually do not report the
sign of their measurements, but only the magnitude. Dr. Girvin realized that
the sign was important, since it provides direct information on the mechanism
of ion transport in superionic conductors. He wrote to all of the experimentalists
in this field (about ten) and asked them the sign of their results, and also a
statement about which sign convention they prefer (i.e. is S plus or minus when
the hot end of the sample is positive?). The experimentalists all replied, and
a consensus emerged regarding signs which Dr. Girvin is recommending be generally
adopted. This survey revealed a number of interesting facts: e.g., two
experimental groups which had claimed to agree on the sign of S in Ag_2HgI_4
actually disagreed because they had adopted different conventions regarding signs.

The sign of S is important because it provides direct information on the
sign of the charge carrier in the solid. Usually the diffusing species (e.g. Ag^+)
is known, thus its sign is known. However, the sign of S can provide information
on the mechansim of disorder--one sign of S is found for interstitial type of
disordering, while lattice gas models predict either sign depending upon the
occupation percentage of the lattice. The situation is very similar to that
found for the Hall effect in semiconductors, where its sign determines the sign
of the carrier. In contrast, the Hall effect in superionic conductors is hard
to measure, and difficult to interpret. Thus the thermoelectric power is the
important measurement for the sign of the charge carrier.

Dr. Girvin also developed some theoretical models for calculating the
magnitude and sign of S. He also corrected the mistakes in previous theories

regarding the sign conventions. One important result was his relating S to the activation energy Δ found for electrical conductivity. Experimentalists had long noted a relationship between S and the thermal activation energy. Dr. Girvin showed that a connection existed of the form

$$- q\ TS = \Delta - \frac{1}{2} E_B$$

where E_B is the polarization energy of the medium, q is the unit of charge, and T is the temperature. He tabulated experimental results, and showed that there existed cases where the polarization energy $\frac{1}{2} E_B$ was significant. This was another important and original contribution to the interpretation of S.

This work on the thermoelectric power by Dr. Girvin has been very well received. It was published in the Journal of Solid State Chemistry. He also was invited to give a number of talks on this subject, both at institutions and international meetings.

b) Ion-Phonon Interactions

During his last year on the grant, Dr. Girvin was particularly concerned with the role of the electron-phonon interaction in many-particle diffusion. At high temperature the phonons are the classical vibrations of the ions around each crystal site. When a particle diffuses to this site, the interaction with the fluctuating ion potential will cause a disruption of its motion. This is the basic cause of electrical resistivity.

One manuscript which was published was "Exact Results for the Quantum Diffusion of Many Particles in a Stocastic Medium" by Girvin and Mahan. There we show that the high temperature particle-phonon Hamiltonian can be solved exactly, even for many-particle systems. An exact solution is possible because the many-particle aspects drop out of the solution. Among the several results we obtain, the most interesting for ion diffusion is that the exact high

temperature limit is merely the Chudley-Elliott model for jump diffusion, which is governed by the equation

$$\frac{d}{dt} P_j = - c(P_{j+\delta})$$

The derivation of this classical formula from the high temperature particle-phonon interaction is non-trivial, and certainly a major result. So at high temperature, most ion systems behave according to the jump diffusion model because of the fluctuating ion field.

c) Transport Anomalies in Random Alloys

Dr. Girvin spent several months collaborating with another research associate, Dr. M. Jonson, and together they have explained a major experimental puzzle in the field of electrical conductivity in disordered materials: the Mooij Correlation. The electrical conductivity in disordered materials is an important topic in superionic conductors, since it provides a description of the electrical properties while the ions are disordering. This is important in electrode materials for batteries.

Mooij was summarizing the thermal characteristics of very resistive materials: random alloys, metallic glasses, etc. He plotted the room temperature resistance $\rho(T)$ of a material on one axis, and its temperature coefficient $\alpha = \frac{d\rho}{dT}$ on another. His curve is shown in Fig. 1a, where each point represents a different alloy or material. The focus of points follow a general trend which is known as the Mooij Correlation: materials with low ρ have a positive α so they get more resistive with increasing temperature. Very resistive materials have a negative α, and become less resistive with increasing temperature. The cross-over behavior of $\alpha = 0$ occurs at a value $\rho^* = 150$ μ-ohm-cm, where the material is temperature independent.

Another illustration of the same physics is shown in Fig. 1b, which shows how materials behave as a function of temperature. Regardless of their

Figure 1

MOOIJ CORRELATION

J.H. Mooij, phys. stat. sol. (a) 17, 521 (1973)
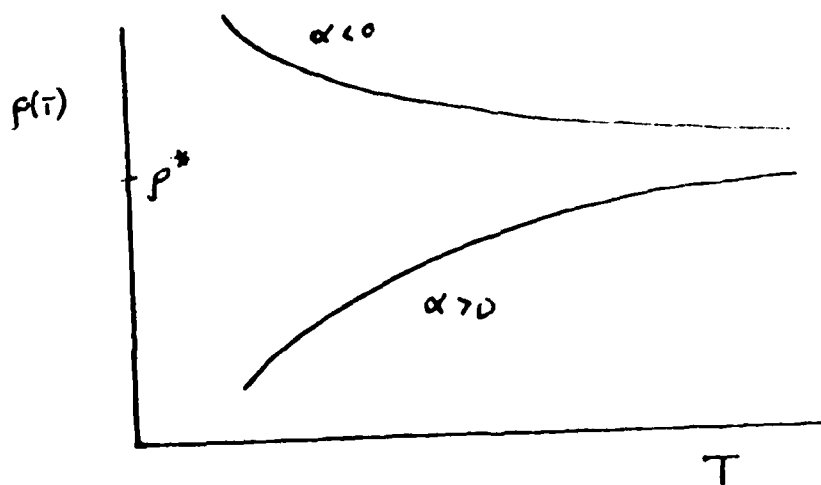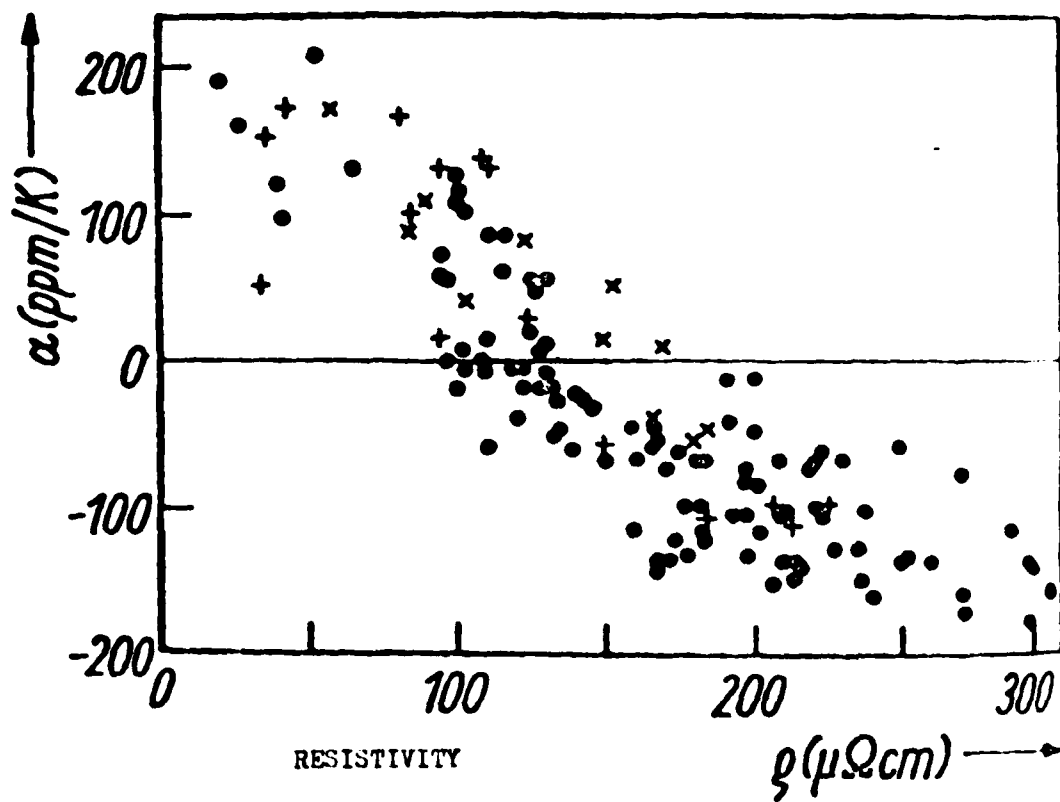
low temperature resistivity, all materials tend towards the same asymptotic value of resistivity which is again ρ^*. L.P. Kadanoff suggested to us that we call this value ρ^*, since it indicates a fixed point. It appears to be a special value. We emphasize that this value is obtained by materials of quite different composition, and different degrees of disorder. The same behavior is found in the A-15 compounds. Thus it appears to be a widespread phenomena. This critical resistivity ρ^* is about a factor of six below Mott's maximum metallic resistivity ρ_{max} = 1000 μ-ohm-cm from localization. Mott-Anderson localization is a low temperature property, whereas the Mooij Correlation is a fixed point in the high temperature resistivity.

The Jonson-Girvin explanation of the Mooij Correlation utilizes the concept of Mott-Anderson localization. Electrons which are almost localized because of disorder diffuse slowly. Thermal fluctuations due to phonons will aid this process, since they provide energy to hop from one quasi-localized site to another. Thus phonons assist the conductivity of quasi-localized electrons. As the temperature is increased, there are more phonons, so the conductivity increases for these electrons. This is the explanation of negative values of α for materials with high values of ρ.

In materials with low values of ρ, the electrons are relatively free to move easily through the lattice. Then the phonons provide a degree of disorder, which scatter the electrons, and impede its progress through the solid. This will cause the resistivity to increase with temperature, and explains the positive values of α for materials with low values of ρ.

Thus phonons play a dual role in the conductivity of electrons. Relatively free electrons travel sufficiently rapidly through the solid that the phonons appear only as Gaussian noise. But relatively localized electrons see the phonons as thermal fluctuations which assist conduction. The competition between these conflicting roles provides the explanation of the Mooij Correlation.

The calculations carried out by Jonson-Girvin used a Cayley tree with random site energies. This model is known to produce Mott-Anderson localization at low temperature with a sufficiently large variation in site energies. They used a variation which was less than this, so that particles would on the average only have a small tendency towards localization. Electron energies in this model were determined through Monte-Carlo Calculations, which used up the annual computer budget for the grant. The phonons were put in by convolution with the phonon spectral function. These calculations are completed, and do show the behavior reported experimentally in Fig. 1a and b. This work was published in Physical Review Letters.

2) Order-Disorder Theory

Superionic conductors are technologically useful because of the high value of ionic conductivity. The ionic conductivity is high because the ions disorder within the solid framework. This ion disordering is what makes them "superionic". We have spent the past several years developing theoretical methods of describing this ion disordering. These are called order-disorder theories.

During the first year of the Grant, 1976-77, we solved the first neighbor order-disorder model for a number of the simple lattice structures which are found in nature, and in superionic conductors. These included the two dimensional lattices such as honeycomb (hc) which is found in the superionic conductor β"-alumina, the planar triangular (pt) lattice found for β-alumina, and the square lattice (sq). In three dimensions, we solved the sc, bcc, and fcc. The fcc is very important, since the silver and copper halides have this close packed structure at room temperature. These phase diagrams, of concentration versus ordering temperature, were calculated by the method of position space renormalization group (PSRG), which is an off shoot of the methods suggested by Wilson and Kadanoff. Our results were often the first obtained for these lattices, and did explain the experimental data of some superionic conductors.

In 1977 we began exploring the relevance of spin one Ising models to the order-disorder theory. We showed that the equivalent lattice gas model could be applied to an important class of superionics: Ag_2HgI_4. These show a first order phase transition when they disorder, although there is no important change in the lattice symmetry. This is explained by our theory as due to the fact that two ion species are disordering at the same time: Ag^+ and Hg^{++}. So each site in the fcc lattice has three possibilities: Ag ion, Hg ion, or empty. These three choices can be assigned the three possibilities of a spin one Ising system, $S = 1, 0, -1$. We then solved for the first time this phase diagram for the antiferromagnetic fcc structure, and predicted that the phase transition in Ag_2HgI_4 is first order, in agreement with experiments. This was the first explanation of this disordering process. We were pleased with the success of this calculation, since it illustrated how modern statistical physics can be used to explain phenomena in superionic conductors.

These calculations take a long time on the computer. Thus they are expensive in both machine time and man hours. This effort has been worthwhile, because of the new results which have been obtained. However, we have also been searching for simpler methods for solving order-disorder theory. Dr. Girvin has been successful in developing a new method which is much easier to calculate, and more accurate than our renormalization group techniques. It uses a self consistent mean field theory, which is still good enough to predict critical exponents (most mean field theories can not do this). His trick is to pick a special quantity for the averaging process. His choice seems far superior to others, and his antiferromagnetic phase boundaries, in a magentic field, are as good as the best available computer results. His method is very simple to calculate, and his reported results were done on a programmable desk calculator. This is an exciting development, since it offers the possibility of doing: (a) better transport calcul ·ions, ⅃ (b) realistic phase boundaries for other superionic conductors.

3) Energy Levels in Silver and Copper Halides

The copper and silver halides constitute a set of superionic conductors (AgI, CuBr, CuI, and CuCℓ under pressure) which have a very simple crystal structure. The AgI system has high ionic conductivity. Furthermore, many better ion conductors are obtained by forming mixed crystals based upon AgI. Nevertheless, the basic reasons that AgI conducts well is not understood. A related question appears to be the propensity of these four compounds to prefer tetrahedral bonding. The related materials AgF, AgBr, AgCℓ have the rocksalt structure, and are not superionic. We decided to spend a year doing a series of calculations to understand why some of these materials prefer tetrahedral bonding, and why they are superionic conductors. Armstrong et al.[4] suggested qualitatively that the filled d-shell of Ag$^+$ and Cu$^+$ provides a unique bonding capability, which could explain this behavior. We think this hypothesis is incorrect, and wish to investigate it with quantitative calculations.

The first step is to understand all of the occupied energy states of the ions in the solid. After that, one can understand how d-states participate in the bonding. So we began a theoretical study of the energy levels in ionic crystals. These can be compared directly with the energy levels observed in a photoemission experiment. However, the photoemission creates a hole in the occupied bands, and this hole has numerous self energy terms which alter its energy over those of the occupied valence bands. So one must be able to calculate all of the hole self energy terms, in order to relate the occupied electron states to the observed photoemission spectra. We have found a method of doing this, which seems to work well.

The first step, which we have just completed, is to test this method on energy levels in the alkali halides. They were chosen for two reasons. First, these materials have been well studied experimentally, so there is an abundance of data

to verify or disprove my theoretical approach. Second, the crystal symmetry of rocksalt and cesium-chloride have an inversion center, which makes all of the mathematical functions in my theory real. For zincblende, the lack of an inversion center makes these function become complex.

The theoretical model we employed, to calculate energy levels, is to assume the holes are localized, and the ions are polarizable points. This model has the virtue that one can solve exactly for all of the self energy terms. Our exact solution derived an energy term which had been overlooked by all previous workers. It arises from the dielectric screening of the Madelung energy. When this term is added to the usual terms of Madelung and Mott-Littleton, we find excellent agreement between calculated energies and experimental data.

Another result we reported was a new interpretation of how the hole self energies due to phonons should be included in comparing theory and experiment for photoemission thresholds. Our calculations found that these self energies are large--contrary to previous speculation--but should not be added to theoretical energies.

4) Born-Mayer Model

The forces between ions are the most important single microscopic property for the behavior of superionic conductors or ionic crystals in general. These forces determine:

a. The crystal structure

b. The degree of ion disordering

c. Diffusion paths and rates

d. Defect structures

e. Sound wave frequencies

This is only a partial list, but does convey the fact that forces between ions are their most important property.

We took the standard Born–Mayer model for the potential between ions, and found the best available parameters for the various attractive and repulsive terms. These forces have been obtained by others by fitting to observed ground state energies, compressibilities, etc. We took these potentials, and asked the computer to find the preferred crystal structure and interatomic separation for all of the alkali, copper, and silver halides. In about half of the cases the forces predicted the wrong crystal structure, and rarely got the right lattice constant to 10%. We tried this with a variety of forces, taken rom different sources. Each set of force constants was equally unsuccessful. We concluded that the standard forces which are the best available are inadequate, and perhaps the Born–Mayer itself is inadequate. We emphasize that these forces are the ones in current usage by experts in the field. We think they are lousy.

Next we re-examined the Born–Mayer model to see whether it had been formulated correctly. We found a term in the ground state energy which had been overlooked by all previous workers. Since the subject is 50 years old, that is quite a long time for a term to be overlooked! Many superionic conductors are tetrahedrally bonded, such as AgI, etc. Our new term applies to such crystals. An ion in a tetrahedral site is sitting in a permanent octupole field. It develops an induced octupole moment proportional to the field, which lowers its energy. The ground state energy is lowered by a term

$$Eg = -\tfrac{1}{2}\alpha_0 O^2$$

where α_0 is the octupole polarizability, and O is the size of the fixed octupole field. The numerical values we find for silver and copper halides are large – on the order of 20 kcal/mol. This is about 10% of the observed binding energy of these crystals. Thus we have found a new term in the crystal binding, which is 10% of the answer! The previous neglect of this term explains why the previously fitted force constants are so poor for these materials.

Among the forces between ions, those which we have not yet mentioned are van der Waals force and those due to ionic polarizability. During the past year we have developed methods of calculating atomic polarizability to an accuracy of 1% using density functional methods. Others have used the same techniques to calculate the frequency dependent polarizability.

We also calculated the van der Waals coefficients C_6 between pairs of ions. These parameters are very important for interatomic forces. Yet values are known very poorly. Our survey of the literature shows that the best values were those of Joe Mayer which were published in 1931. Fundamental calculations by quantum chemists are limited in numerical accuracy, and only apply to atoms of small atomic number. Experimental data is only available for rare gases. Thus there are no experimental values, and only very old empirical ones, for these parameters. Recent empirical sets seem less reliable than Mayer's.

We calculated C_6 with an accuracy of several per cent. We used the fact that the value of C_6 between any two ions ℓ & j is given by the convolution of their polarizabilities at complex frequencies

$$C_6 = \frac{3}{\pi} \int_0^\infty du \; \alpha_\ell(iu) \; \alpha_j(iu)$$

Since we can calculate the polarizability to 10% accuracy for real frequencies, we were also able to calculate them for an imaginary frequency.

5) __Properties of Ag_2S, Ag_2Se, and Ag_2Te__

Professor Kobayashi, during the year he was supported on the Grant, developed a theory of the electronic properties of the silver chalcogenides. These interesting superionic conductors are known to be semiconductors in which the ion density, and the electron (or hole) density, can be varied continuously by an external voltage. The ions are quite mobile, so they are a superionic conductor. The electronic properties are typical of a semiconductor, but of special interest to us because the material is a good superionic conductor.

The theoretical model is based upon the premis that only long range fluctuations affect the optical and electrical properties. They derived a continuum model of long wave length fluctuations, which was made self-consistent. The parameters of the theory are readily measurable quantities such as the speed of sound, or the dielectric constant or refractive index. With this model they are able to calculate many measurable quantities such as the dc conductivity, ac conductivity, Raman scattering, etc. These all agree quite well with the experimental measurements.

B. Publications

1) S.M. Girvin and G.D. Mahan, "Cation Disordering Ag_2HgI_4 amd Cu_2HgI_4",
    Solid State Comm. <u>23</u>, 629 (1977).

2) S.M. Girvin, "Thermoelectric Power of Superionic Conductors", J. Solid
    State Chem. <u>25</u>, 65 (1978).

3) G.D. Mahan and S.M. Girvin, "Blume-Capel Model for pt and fcc Lattices",
    Phys. Rev. <u>B17</u>, 4411 (1978).

4) S.M. Girvin, "New Method for the Ising Model Phase Diagram", J. Phys. <u>C11</u>,
    L427 (1978).

5) S.M. Girvin, "Critical Conductivity of the Lattice Gas", J. Phys. <u>C11</u>,
    L751 (1978).

6) S.M. Girvin and G.D. Mahan, "Thermoelectric Power in Half-Filled Bands",
    Phys. Rev. <u>B19</u>, 1302 (1979).

7) M. Jonson and S.M. Girvin, "Electron-Phonon Dynamics and Transport Anomolies
    in Random Metal Alloys", Phys. Rev. Lett. <u>43</u>, 1447 (1979).

8) S.M. Girvin and G.D. Mahan, "Exact Results for the Quantum Diffusion of Many
    Particles in a Stocastic Medium", Phys. Rev. <u>B20</u>, 4896 (1980).

9) G.D. Mahan, "Photoemission in Alkali Halides: Energies and Lineshapes",
    Phys. Rev. <u>B21</u>, 4791 (1980).

10) S.M. Girvin and M. Jonson, "Dynamical Electron-Phonon Interaction and
    Conductivity in Strongly Disordered Metal Alloys", Phys. Rev. <u>B22</u>, 3583 (1980).

11) G.D. Mahan, "Covalent Bonds in Ionic Crystals", Chem. Phys. Lett. <u>76</u>,
    183-185 (1980).

12) G.D. Mahan, "van der Waals Coefficient Between Closed Shell Ions", J. Chem.
    Phys. (Scheduled January, 1982).

13) M. Kobayashi, F. Sukegawa, and I. Yokota, "Response Functions, Relaxation
    Time, and Conductivity of Silver Chalcogenides", Solid State Ionics (in press).

C. Invited Talks on Grant Research

G.D. Mahan
    Midwest Solid State Physics Conference, Argonne, October 1978
    Seminar, University of Chicago, February 20, 1979
    Seminar, Oak Ridge, June 6 & 7, 1979
    Seminar, Argonne National Laboratory, December 3, 1979
    Seminar, IBM San Jose, January 8, 1980
    Seminar, Kentucky, April 24, 1980

S.M. Girvin
    Midwest Solid State Theory Symposium, Ford Research Center, October 9, 1979
    Seminar, Pennsylvania State University, November 30, 1978
    Seminar, Washington University, St. Louis, February 14, 1979
    Seminar, University of Michigan, February 27, 1979
    Seminar, National Bureau of Standards, March 1, 1979
    Seminar, University of Southern California, March 5 & 6, 1979
    Seminar, Iowa State University, March 8, 1979
    Seminar, Boston University, March 19, 1979
    Seminar, Bell Telephone Laboratories, April 17, 1979

D. Personnel

Dr. Steven M. Girvin was a full time research associate on the Grant from
January 1, 1977 until August 31, 1979. He now has a permanent position with
the National Bureau of Standards in their research division.

Dr. Michisuke Kobayashi was a research associate supported by the Grant from
August 1, 1980 until July 31, 1981. He was on a one year leave from his
permanent position as a faculty member at Niigata University in Japan.

Mr. Paul Draper, Graduate Student, was supported on the Grant during the summers
of 1980 and 1981. He has a B.A. and M.A. degree from the University of Kansas,
and he is working on his Ph.D. at Indiana University. He did several calculations
of atomic polarizability using a new method invented by the principle investigator.